

To the students of Virtual glass course on Physical Properties of Glass

Dr. Varshneya's note (October 11, 2008):

I follow my book, "Fundamentals of Inorganic Glasses" very closely when I teach. Because of my legal Agreement with the publisher, I am unable to provide you downloadable (high resolution) figures and text for the lectures. Please have a copy of the book handy while I lecture, or at least consult afterwards. To those of you who have little or no access to the book, I am providing some of the material in outline form.

I regret the inconvenience, but, please understand.

# Advanced Vitreous State – The Physical Properties of Glass



*Saxon Glass Technologies, Inc.*

## Strengthening of Glass

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Advanced Vitreous State - The Properties of Glass: Strengthening of Glass

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## Techniques of strengthening

- (1) reduce the severity of the flaws (reduce  $K_I$ );
- (2) control of environment in the immediate vicinity of the crack tip (increase  $K_{Ic}$ );
- (3) polymeric coatings to reduce risk of surface damage (reduce  $c$ );
- (4) introduce compression in the surface (increase  $\sigma_a$  to reach  $\sigma_f$  level)
- (5) crack pinning, deflection or crack-tip shielding (increase  $K_{Ic}$ ).

**Firepolishing** or **etching** with 2 –6% HF (or ammonium bifluoride) is the best way to reduce the severity of flaws. (Not very permanent.)

- Polymer coatings, UV-cured polyacrylates act as barrier to reduce the activity of the corrosive environment.
- “Hot end” coatings:  $\text{SnCl}_4/\text{TiCl}_4$  vapors deposit hard coatings of  $\text{SnO}_2$  and  $\text{TiO}_2$  to reduce risk of abrasion. Mostly replaced by dip or spray of “cold-end” coatings of stearates, oleates (soaps) and dilute polyurethane/water solutions. Increased lubricity reduces abrasion.
- Compressive stresses in the surface are helpful because any applied tension must exceed this compression level and fatigue limit before sub-critical crack growth can occur.
- (Surface flaws are usually the more fatal)
- Thermal tempering
- Ion exchange strengthening (“ion stuffing”; “chemical tempering”)
- Low expansion glazing of surface
- Surface crystallization

## Development of permanent stresses in glass

- Mechanism 1: Viscoelastic or Frozen temperature gradient

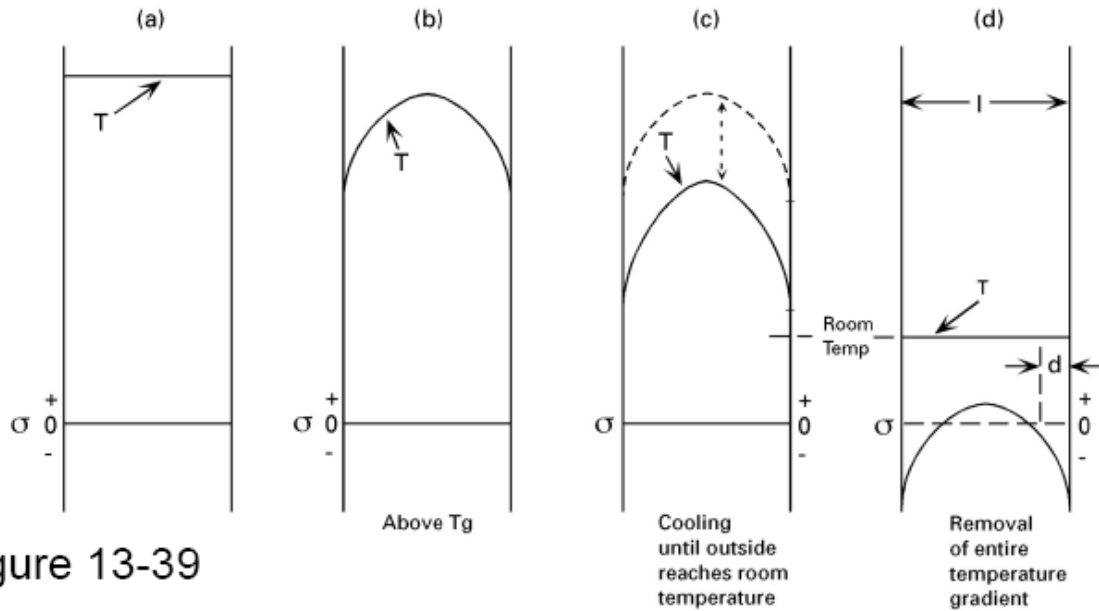


Figure 13-39

The actual cooling profiles do not matter. Why?

## Mechanism 2b: Transient structural heterogeneity

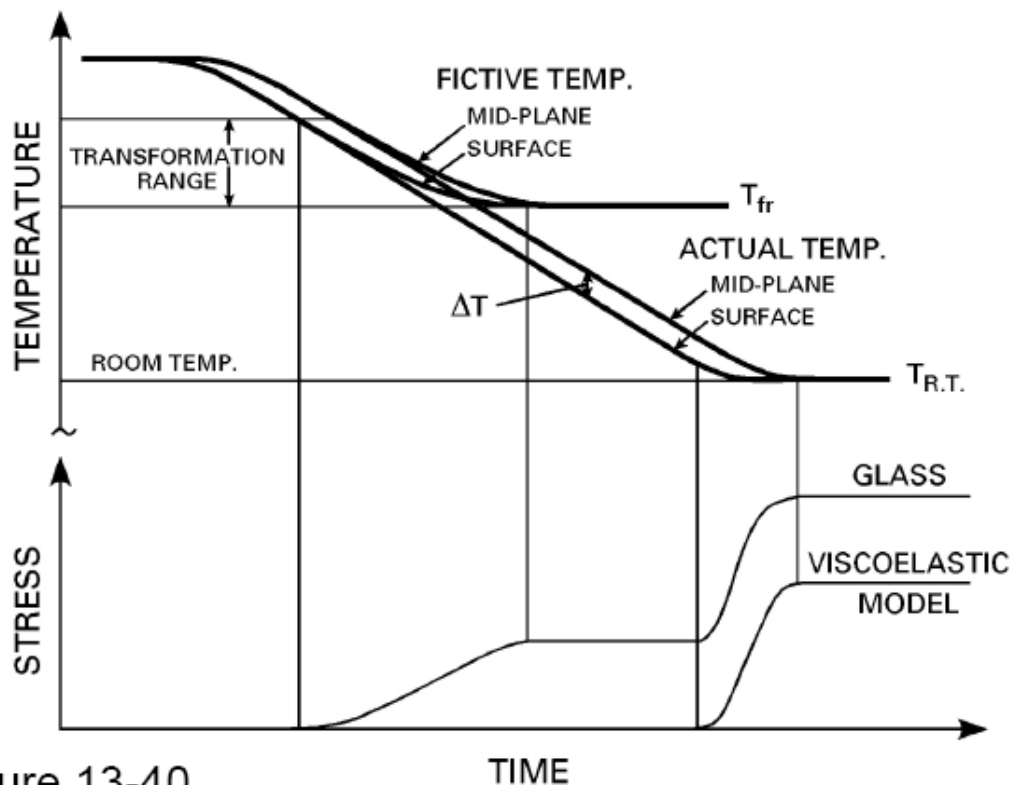


Figure 13-40

### Summary of stress development principle:

- Permanent stress develops because different layers of glass start with a built-in temperature gradient (outside cooler than the inside) and go through the glass transition range not only at different cooling rates but also at different instants of time.
- **Basic rule of thumb: Part that cools last is in tension.**

## Thermal stress distribution

- (1) Compression on the outside; tension on the inside.
- (2) If heat extracted is slowly, say by natural cooling, then temperature distribution, hence stress distribution are parabolas.
- (3) Compression area = tension area
- (4) Compression magnitude = 2 x tension magnitude
- (5) Location of neutral axis below surface is about 1/5th of total plate thickness. ("Case depth"). About 1.2 mm for 6 mm plate.

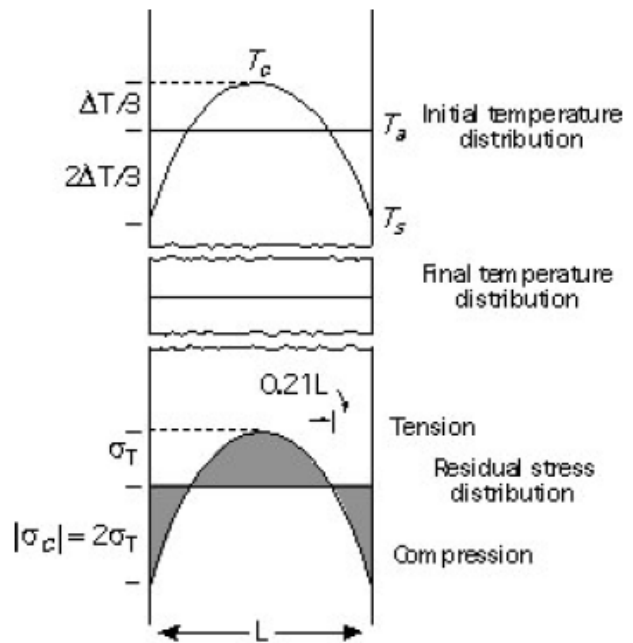
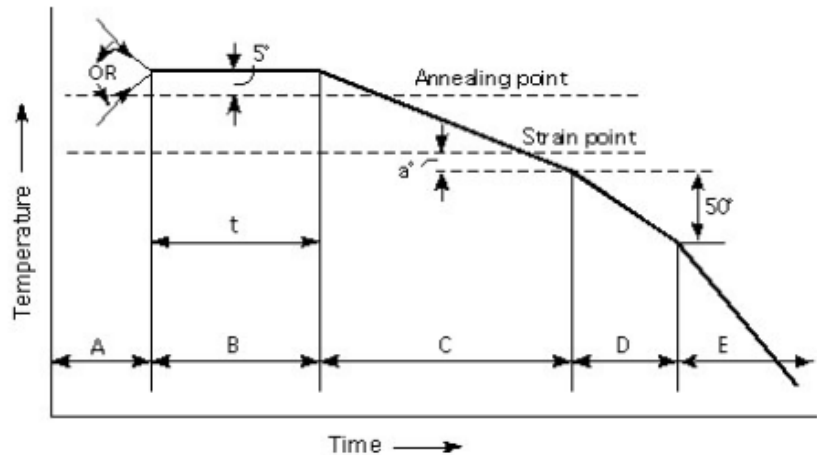


Figure 13-43

## Annealing

Removal of stress  
Structural homogenization

Figure 13-46



A (heating rate)	$= 500/[\alpha d^2]^{\circ}\text{C}/\text{min}$
B (holding time, $t$ )	$= 15z$ min for cooling from one side; $= 30d$ min for cooling symmetrically
C (slow cool)	$= 42.6/[\alpha d^2]^{\circ}\text{C}/\text{min}$
$a^{\circ}$ ( $^{\circ}\text{C}$ below strain point)	$= 5^{\circ}\text{C}$ for 0.3 cm thick plate $= 10^{\circ}\text{C}$ for 0.6 cm thick plate $= 20^{\circ}\text{C}$ for 1.3 cm thick plate
D (Fast cool)	$= 2$ times the slow cool
E (final cool)	$=$ no greater than 10 times the slow cool (13.95)

where  $\alpha$  = thermal expansion coefficient of glass in  $10^{-7}/^{\circ}\text{C}$  units;  $z$  = thickness of the glass (cm);  $d = z$ , when heated/cooled from one side only; and  $d = z/2$ , when heated/cooled symmetrically from both sides.

## Science of chemical strengthening (summary)

- Diffusion kinetics
  - o Exchange of ions on one-to-one basis.
  - o Interdiffusion coefficient given by Nernst-Planck expression. Approximated by simple error function
  - o Influence of generated stress
- Stress generation (due to ion size difference)
  - o One-dimensional difference between the molar volumes of equimolar alkali glasses as a function of local composition. (Linear network dilatation coefficient. Similar to linear thermal expansion coefficient).
- Stress relaxation
  - o Viscous flow
  - o Accommodation of size difference by plastic deformation

## Mathematics of stress development by ion exchange

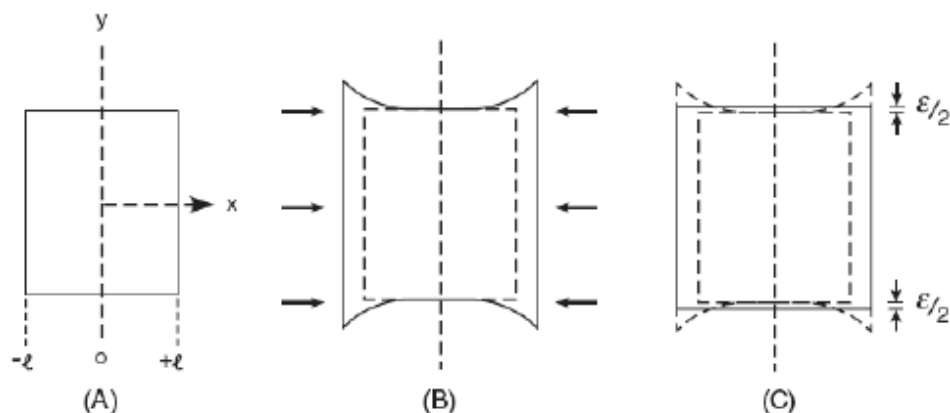


Figure 14-12. Dimension changes after ion exchange.  
(A) No ion exchange. (B) Ion exchanged and unrestrained.  
(C) Ion exchanged and restrained.



$$(e_y)_x = (e_z)_x = \left[ \frac{1}{(2L)} \right] \int_{-L}^{+L} (BC)_x \, dx \quad (14.51)$$

The true strain of an  $x$ -element, however, is the difference between the equilibrium and the net expansions, i.e.

$$(e_y)_x = (e_z)_x = (BC)_x - \left[ \frac{1}{(2L)} \right] \int_{-L}^{+L} (BC)_x \, dx \quad (14.52)$$

The stresses  $\sigma_{ii}$  are, hence, given by

$$(\sigma_{zz})_x = 0, \text{ and}$$

$$(e_{yy})_x = (e_{zz})_x = \left[ \frac{(BC)_x E}{(1-\nu)} \right] - \left[ \frac{E}{\{2(1-\nu)L\}} \right] \int_{-L}^{+L} (BC)_x \, dx \quad (14.53)$$

where  $E$  is the Young's modulus and  $\nu$  is the Poisson ratio. If  $E$ ,  $\nu$ , and  $B$  do not vary with composition then the expected stress profile follows the concentration distribution  $C_x$ . The average concentration given by the integral on the RHS is generally quite small for a 2–3 mm thick glass plate. Thus, in the interior as  $C \rightarrow 0$ ,  $(\sigma_{yy})_x \rightarrow$  small tension corresponding to the RHS in eq. (14.53). On the surface, however,  $(\sigma_{yy})_x \rightarrow$  large compression because of the large value of  $BC$  at  $x = \pm L$ . Note that:

$$\int_{-L}^{+L} (\sigma_{yy})_x \, dx = 0$$